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DEPARTMENT OF CERAMICS

A. V. BLEININGER, Director

THE EFFECT OF ACIDS AND ALKALIES UPON CLAY IN THE PLASTIC STATE

BY

A. V. BLEININGER AND C. E. FULTON

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R. K. HURSH

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THE EFFECT OF ACIDS AND ALKALIES UPON CLAY IN THE PLASTIC STATE.

A. V. BLEININGER AND C. E. FULTON, Urbana, Ill.

INTRODUCTION.

The effect of acids, alkalies and salts upon clay suspensions (slips) has been discussed frequently, and the work of Simonis, Mellor, Rieke, Boettcher, Ashley, Foerster and Bollenbach deals with the viscosity and other phenomena of systems in this state. But little is known concerning the effect of such reagents upon clays in the plastic condition which differs from that of a suspension, due to the cohesive influence of the particles upon each other.

It has been realized for some time that the properties of clays in the wet state are influenced by the presence of alkalies and acids. Seger explains the increase in the plasticity of clay upon storing by the assumption that the fermentation of organic substances results in acids which neutralize the alkalinity due to the decomposed feldspar, and in addition bring about the "sour" condition which accompanies the improvement in working qualities. Rohland¹ discusses this subject from the theoretical standpoint and makes quite definite statements with reference to the principles underlying the effect of various reagents upon clays in the plastic state. He arrives at the conclusion that the plasticity of clays is increased by the presence of H^+ ions, while, on the other hand, the OH' ions are active in the opposite direction. According to Rohland, the plasticity is likewise increased by the addition of colloids like tannin, dextrine, etc., as has been shown by the work of Acheson, fine grinding and the storage of the clay in cool and moist places. It is supposed that the increase in plasticity is coincident with the coagulation which is primarily due to the presence of the hydrogen ions; it is retarded by the hydroxyl ions. The salts of strong bases and weak acids which dissociate OH' ions hydrolytically produce an effect similar to that of the hydroxyl ions. Neutral salts, Rohland goes on to say, with but few exceptions, are indifferent in their

¹ "Die Tone," pp. 35-19.

effect, though some appear to show a contradictory behavior, which has not yet been explained. "The effect of the hydroxyl ions may be weakened, compensated or strengthened by the action of the salt in question. Thus borax is an example of the first class and sodium carbonate of the second."

The same writer further says that with some clays the addition of Na_2CO_3 brings about an improvement in plasticity, while ordinarily the same reagent behaves in the opposite sense, due to the hydrolytic dissociation of OH' ions. It is possible that the effect of hydroxyl ions might be neutralized by the CO_3'' ions.

DRYING SHRINKAGE.

A decided lack of data exists with reference to the determination of the effect of reagents upon the plasticity of clays. It was thought advisable for this reason to begin work along this line without reference to any theoretical speculations. The most obvious criterion to be used in this connection is the drying shrinkage, which, from what we know of the properties of clays, is a function of plasticity. It is evident that any effect caused by the addition of reagents will at once be indicated by the shrinkage of the clay.

In this series of experiments Georgia kaolin was used. This clay was found to show an acid reaction when tested with phenolphthalein. This would indicate that the addition of acid should bring about no decided change in the clay, a fact which was verified by experiment. The reagents employed were HCl , H_2SO_4 , NaOH and Na_2CO_3 . In carrying out the work a thoroughly mixed sample was first prepared so that variations due to differences in composition were reduced to a minimum. The test specimens were in the shape of bars $3\frac{5}{16} \times 1 \times \frac{5}{8}$ inches. Even the most careful linear shrinkage measurements by means of the vernier caliper were found to be unsuitable for the work. A volumometer permitting of readings to 0.05 cc. was then employed. The measuring liquid used was petroleum from which the lighter oils had been expelled by heating. The bars were at once weighed and allowed to dry at the laboratory temperature for three days, after which they were heated at 110° to constant

weight, and their shrinkage determined. For each concentration of reagent three bars were made and measured.

Clay and Water.—A study was first made of the drying shrinkage of the clay with different amounts of water, ranging from the soft state in which the clay could be barely molded to the condition of minimum water content when molding was likewise difficult for the opposite reason. The shrinkage relations to the various contents of water are shown in Fig. 1. The third point on the curve, showing a shrinkage of 10.45 per cent. with a water content of 32.8 per cent., represents the most workable state. Any increase in water above this point is at once observed by the rapid softening of the mass. The clay hence is well suited for the work at hand, owing to the ease with which the condition of best working behavior is recognized in distinction from many other plastic clays which possess a long working range.

Effect of Acid.—Upon adding from 0.025 to 0.525 gram of hydrochloric acid to 100 grams of clay, we observe from Fig. 2 that the shrinkage is not materially affected by this reagent. While two maxima of somewhat greater contraction are noted, the principal result seems to be a reduction in shrinkage, contrary to what might be expected from Rohland's statements. The fact remains, however, that conditions are more complex than they seem, due to the probable solution of various salts in the clay as well as the formation of some chlorides by the acid.

It was thought that further insight into the effect of the acid might be obtained by calculating the total and the shrinkage water in terms of the true clay volume, *i. e.*, weight divided by the density of the powdered substance, according to the relation:

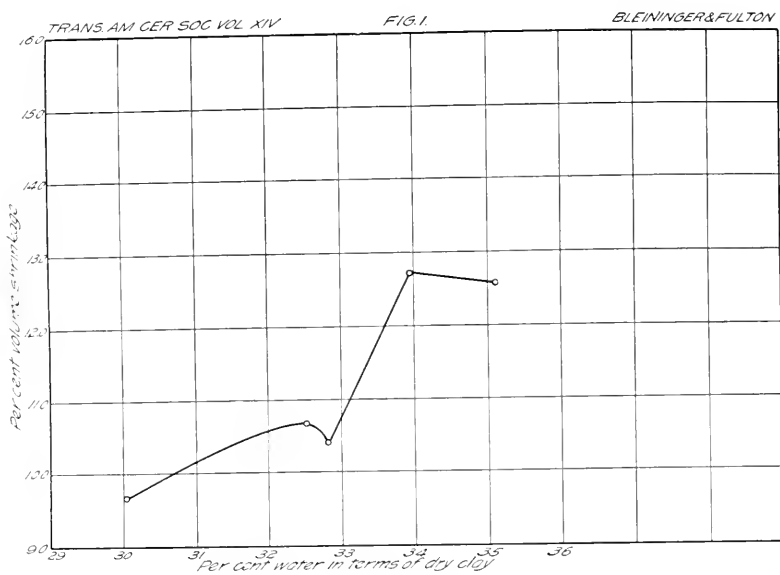
$$100 \frac{(v_1 - v_2)}{\frac{w}{d}} = \text{per cent. (by volume) shrinkage water.}$$

Where v_1 = volume of wet brickette,

v_2 = volume of dry brickette,

w = weight of brickette, dried at 110° C.,

d = density of the dry and powdered clay.



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FIG 3

BLEININGER & FULTON

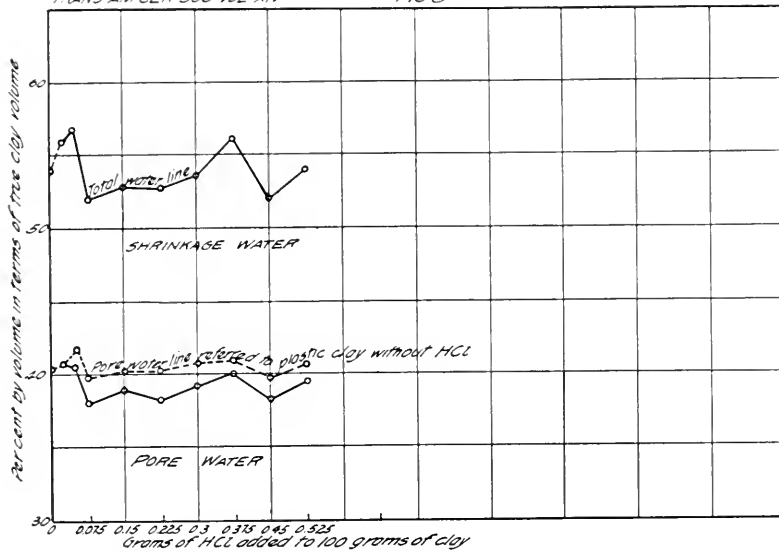
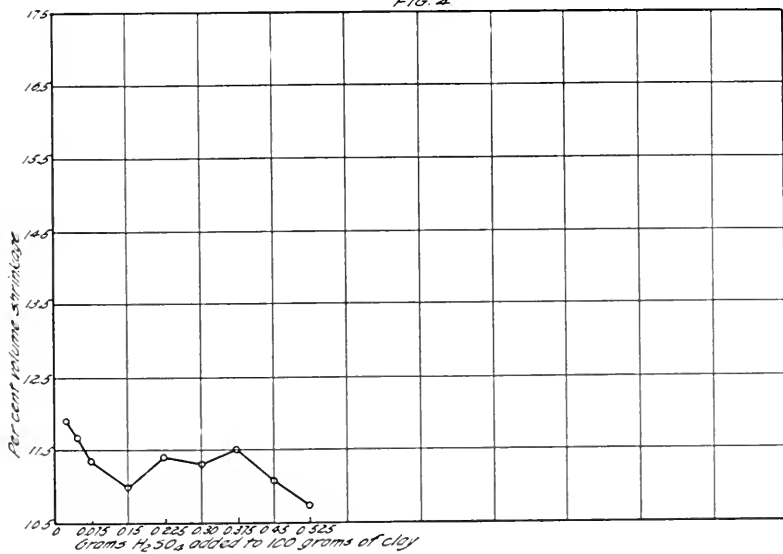
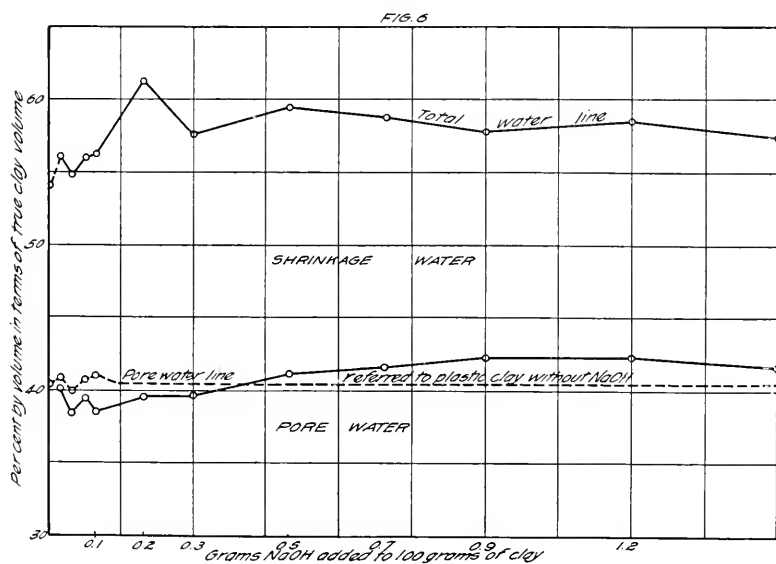
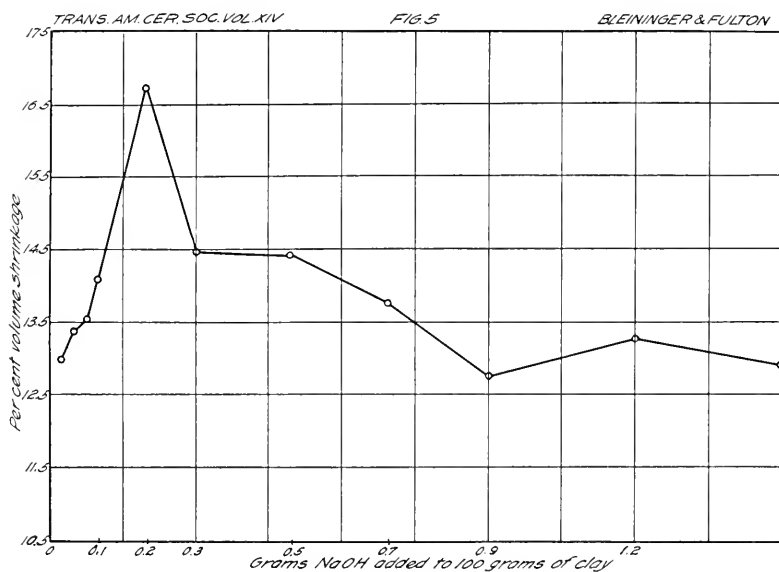
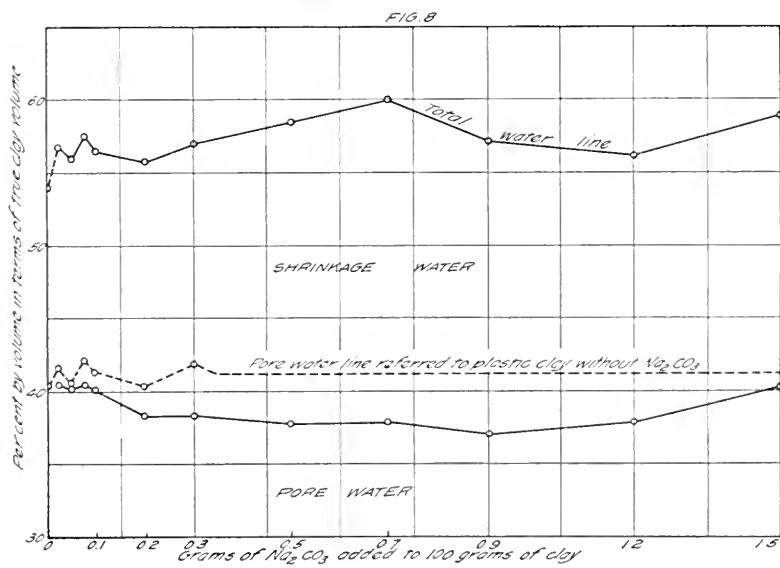


FIG. 4







Similarly, the volume of the total water in terms of the true clay volume is calculated.

In the diagram of Fig. 3, the respective volumes of total and shrinkage water are shown. The boundary between the volumes of water and that of clay is, of course, the line representing zero water and 100 volume per cent. of clay. It is shown in Fig. 3 that the content of pore water has been decreased, that of the shrinkage water having been increased both at the expense of the pore water and due to the rise in the total water content at the two max. points.

The addition of sulphuric acid likewise tends to decrease the shrinkage as is shown in the diagram of Fig. 4.

Effect of Alkalies.—The influence of NaOH is illustrated in the diagram of Fig. 5. It is at once noted that with 0.2 per cent. of this reagent a striking max. point is reached, indicating a marked increase in shrinkage, contrary to what we should expect according to Rohland's views. Only after adding larger amounts does the contraction descend towards the normal value. Here again, according to Fig. 6, the increased shrinkage is due in part to the specific effect of the reagent in increasing the distance between the particles in the plastic state and, in part, to the denser structure of the clay upon drying. Beyond the max. point this condition changes, since the pore water line rises above the normal level. Since, at the same time, the total water line descends, the shrinkage is gradually decreased. The structure of the dried clay is thus more open with the higher contents of NaOH than with the smaller additions.

The growth in shrinkage is still more pronounced in the case of Na_2CO_3 , Fig. 7, a phenomenon contrary again to Rohland's statements, although, of course, in this case the effect of the CO_3 ion might have proven a factor, especially if absorption has taken place to any appreciable extent. However, even under this assumption, it is somewhat improbable that the carbonic acid could have brought about such a change where other acids failed to accomplish anything like the same result. In this diagram the maximum occurs with 0.7 per cent. of the reagent. With larger concentrations the shrinkage is again reduced, but appears to gain once more with amounts beyond 1.2 per cent.

As may be observed from the diagram of Fig. 8, the pore water volume is diminished throughout this series with a gradually increasing total water content up to the maximum.

DEFLOCCULATION SERIES.

It was thought desirable to study the effect of the acids and alkalis upon the clays as regards deflocculation, using solutions of the same concentration present in the plastic clay, as shown by the preceding curves. To illustrate: If to 100 grams of clay, requiring 34.9 per cent. of water, 0.025 gram Na_2CO_3 was added, this would represent a solution carrying $0.025 \div 34.9 = 0.000716$ gram Na_2CO_3 per cubic centimeter of water. Such solutions

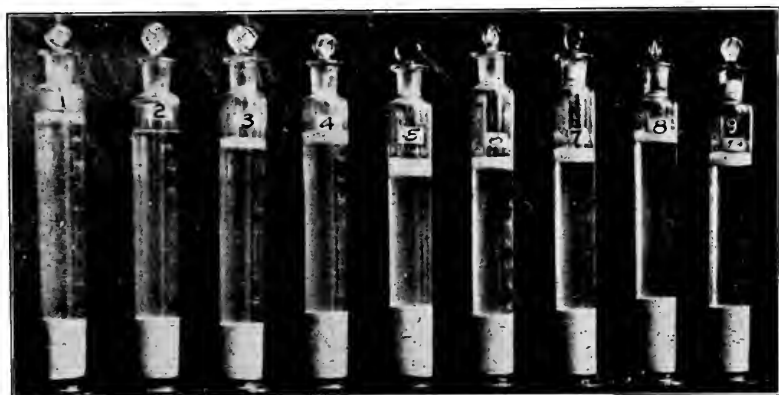


Fig. 9.

No.	Wt. clay. Grams	Wt. Na_2CO_3 . Grams	Water, cc.	Volume of sediment, cc.	Condition of turbidity of supernatant liquid
0	5	...	98	18.0	Clear
1	5	0.0713	98	19.5	"
2	5	0.1423	98	21.8	"
3	5	0.2296	98	24.3	"
4	5	0.4529	98	28.0	"
5	5	0.6803	98	27.4	"
6	5	0.8913	98	28.0	"
7	5	1.0659	98	28.0	"
8	5	1.3549	98	28.0	"
9	5	1.5511	98	28.0	"

were made up of concentrations corresponding to the various points in the preceding curves. In each case to 5 grams of clay 98 cc. of the solution were added in a graduated tube. The tubes were placed in a shaking machine for 90 minutes and allowed to stand. It was found that the clay itself, without any reagent, settled well, showing a clear, supernatant liquid and a sediment occupying 18 cc.

It was shown that the addition of acid produced no change, excepting in the volume of the sediment, which was finally increased from 18 to 28 cc., as is observed from Fig. 9.

The sodium carbonate solutions, on the other hand, started with conditions of complete deflocculation (Fig. 10). The sediment volumes are shown in the table accompanying each figure.

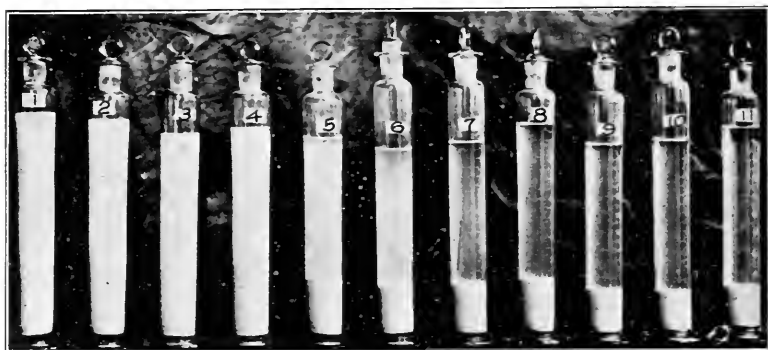


Fig. 10.

No.	Wt. clay, grams	Wt. Na_2CO_3 , grams	Water, cc.	Volume of sediment, cc.	Condition of turbidity of supernatant liquid
0	5		98	18	Clear
1	5	0.0702	98	4.5	Very turbid
2	5	0.1426	98	19	Very turbid
3	5	0.2090	98	24	Slightly less turbid
4	5	0.2822	98	24	Less turbid
5	5	0.5713	98	20	Slightly turbid
6	5	0.8388	98	20	Slightly turbid
7	5	1.3642	98	21	Almost clear
8	5	1.8571	98	19	Clear
9	5	2.5059	98	18	Clear
10	5	3.4006	98	18	Clear
11	5	4.0709	98	18	Clear

The maximum point of the shrinkage curve corresponds to tube No. 8, where the supernatant liquid is clear for the first time.

CONCLUSIONS.

The writers do not attempt at this time to explain the phenomena on theoretical grounds. It is evident that the conditions are quite complex and in order to explain them still further modes of attack must be sought for. The rules laid down by Rohland do not seem to apply, since in the main the acids clearly caused shrinkage to decrease while the alkalies produced the reverse effect, which is contrary to his statements. In order to be fair, however, attention must be called to the fact that shrinkage in this work has been considered a measure of plasticity, while Rohland speaks of plasticity itself without attempting to correlate this property with any numerical value. As is well known, there is at the present time no clear conception as to the relation between plasticity and shrinkage excepting the general fact that the plastic clays as a class show a greater drying shrinkage than the leaner ones.

DISCUSSION.

Mr. R. J. Montgomery: I should like to ask Prof. Bleininger how long those slips in the cylinders had stood when the photographs were taken.

Prof. Bleininger: Twenty-four hours. I might add also that in making the volume determinations they were stored twelve hours in a moist chamber in order to bring about some sort of an equilibrium between the clay and the reagent.

Mr. Kerr: I should like to raise the question as to what determinations, if any, were made of the electrolytes present in the clay before the acids and alkalies were added. Was any general data obtained upon this point?

Prof. Bleininger: No direct determination was, of course, made. However, you have seen the series of tubes which ought to indicate pretty clearly to one familiar with this work whether the initial conditions are acid or alkaline. We are principally endeavoring to get at the experimental facts without much regard to theoretical assumptions. The evidence so far obtained along these lines is not sufficient to base upon it any definite

line of procedure. The work of Veimarn especially has disturbed previous conclusions by his very startling claims with reference to colloids. We thought it wise to work along the lines which I have indicated.

Mr. Kerr: The only point which I wished to bring up was that if one clay contained positive ions in excess and another clay negative, the addition of either acid or alkali to one clay would not correspond to a similar addition to the other clay. Some clays give a strongly acid reaction, others a weakly acid, while still others are somewhat alkaline. Data upon neutralization might be included.

Prof. Bleininger: This is brought out in the deflocculation experiments. At the same time corrections work very well in theory, but when you come to make them you will find that neutralization does not necessarily follow. I, of course, want to check Mr. Ashley's work in this investigation in a general way. I realize we have learned a good deal from his work and I want to say that he is to be given great credit for having started work of this kind.

Mr. Purdy: I would like to ask if any experiment has been made to determine whether, as a rule, trivalent electrolytes coagulate clays more readily than do the uni- and divalent salts.

Prof. Bleininger: I would say that it has been done with various materials.

Mr. Purdy: Has it been done with clays? I would like to see some experiments tried on that and reported, because I have been unable to show that the trivalent salts have any more effect than the other. That is one of the respects in which the clay is different.

Prof. Bleininger: Mr. Ashley, of course, has done such work.

Mr. Purdy: That is what he did not do, he accused himself on that point.

Prof. Bleininger: I think he did work with phosphates. Of course, as I said before, this work is being continued and we expect to take representative reagents.

Mr. Kerr: What measurements other than volume shrinkage were made?

Prof. Bleininger: We hope to take up various things in

time. One of them is a vapor tension investigation, for which a special apparatus is now being designed.

Prof. Grout: I would like to ask if the curves which are drawn there, such as the first curve which you show on the screen, were the average of a series of results on one clay or just one series of tests.

Prof. Bleininger: Taken as the average of three determinations in each case.

Prof. Grout: I wondered if that approximation of a maximum was so characteristic that you could report it for publication on one series of tests; whether your area of determination was not such that you might not safely report it.

Prof. Bleininger: Well, we were able to get very good checks, also we notice that the two acids are behaving very similarly. We recognize, however, that there are a good many factors involved which it is almost impossible to correlate in a technical investigation of this kind. Of course, if we were to carry on this investigation from a strictly physical chemical standpoint, we would proceed along somewhat different lines.

Mr. Potts: I would like to ask Prof. Bleininger just what practical application he expects to make of that treatment. Does he propose to make kaolins plastic?

Prof. Bleininger: I haven't any idea as to what this information could be used for and am indifferent in regard to that point.

NOTE ON THE DISSOCIATION OF CALCIUM HYDRATE.

By R. K. HURSH.

INTRODUCTION.

The present study, which was intended to be of a technological rather than of physical-chemical nature, was undertaken with the purpose of learning more regarding the properties and behavior of the compound $\text{Ca}(\text{OH})_2$. The work has a practical bearing in demonstrating the value of methods of thermal study upon problems dealing with the dehydration of limes, cements and plasters.

A number of values have been given for the dissociation temperature of calcium hydrate. Herzfeld¹ says that dissociation evidently begins at 470° to 500° C. He gives the thermal effect of slaking CaO as 1.51 cal. per gram of $\text{Ca}(\text{OH})_2$ and the maximum temperature of formation as 468° . H. Rose² found that pure calcium hydrate lost nothing at 100° C., absorbed CO_2 at 200° and 300° , and began to lose H_2O at about 400° C.

Le Chatelier³ gives a vapor tension of 100 mm. at 350° C., and 760 mm. at 450° C.

Tichborne⁴ found the precipitate from a heated solution of lime water to show a loss on blasting that corresponded to the formula $3\text{CaO} \cdot 2\text{H}_2\text{O}$. Others using similar methods failed to find such a hydrate.

Dr. Johnston,⁵ whose work is taken up further on, found the dissociation pressure of $\text{Ca}(\text{OH})_2$ to reach 760 mm. at 547° C.

METHODS AVAILABLE.

There are several methods of studying the dissociation of hydrates, such as the making use of heating curves, the determination of the aqueous pressure in direct or differential tensimeters, and the method depending upon the determination of the loss of weight at different temperatures

¹ Handbuch der anorg. Chem., C. Dammer.

² Pogg. Ann. du Physik u. Chem., LXXXVI, 105.

³ Handbuch der anorg. Chem., 22, Gmelin-Kraut.

⁴ Chemical News, XXIV, 199.

⁵ Ztschr. phys. Chem., LXII, 330.

HEATING CURVE METHOD.

A portion of the substance is placed in a furnace with a thermocouple touching it and another near it. The furnace is heated, and the temperatures of the furnace and substance are noted. At the point where dissociation takes place, a lag may be noted in the heating curve due to the endothermic reaction, *i. e.*, the absorption of heat due to the expulsion of water. It is frequently difficult and sometimes impossible to determine the point by this means, owing to the small amount of heat required for the reaction of the slow rate of dissociation. Distinction may be made between mechanically held or dissolved water and chemically combined water. In the case of chemical water, the lag will occur abruptly at the temperature of dissociation. Mechanical or dissolved water will pass off gradually over a range of temperature, and the lag due to these is gradual, showing no abrupt break at a definite temperature.

In the use of heating curves, close regulation of the temperature is very necessary to get reliable results. There should be no fluctuations in the heating of the furnace. Three general methods may be followed in the heating:

Indiscriminate, in which no attention is given to the rate of the furnace curve, and only the lags in the heating curve of the substance are given attention.

Constant rate, in which the temperature of the furnace is raised at a uniform rate.

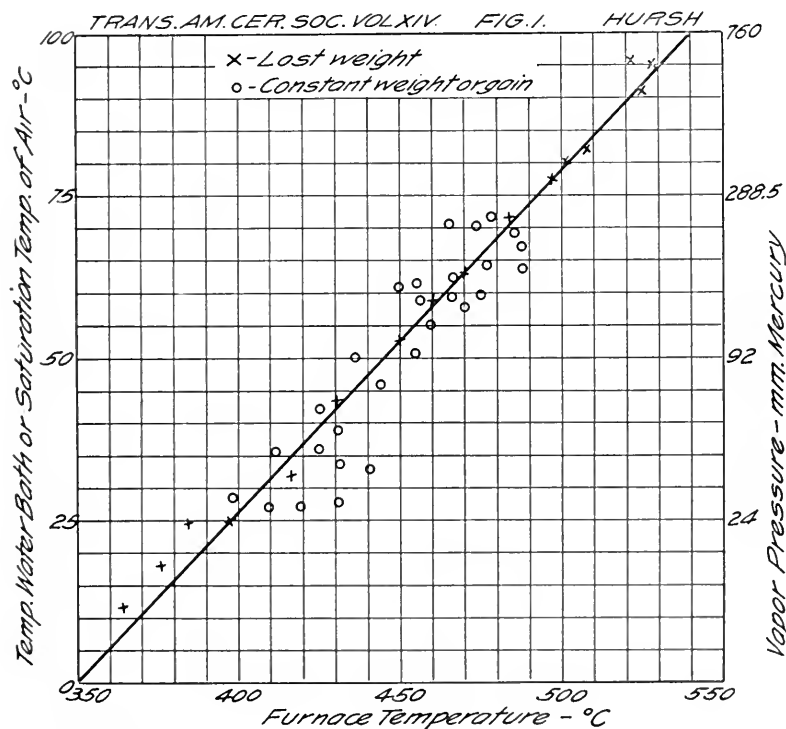
Constant difference, in which a uniform difference between furnace temperature and that of the material is maintained. This method is the best, although the most difficult one of the three. The constant rate method gives good points, but the lag will, in most cases, be sloped instead of horizontal.

AQUEOUS PRESSURES METHOD.

Van Bemmelen, in studying the dehydration of the silicic acid gel, placed his samples in desiccators containing various concentrations of H_2SO_4 . Constant temperature was maintained, and the samples were kept in the desiccators for sufficient time to reach equilibrium under the various vapor tensions. By plotting the loss of weight curve for the several concentrations of H_2SO_4 or the corresponding vapor pressures, he was able to

determine the inversion points and the degrees of hydration in each case. The same method has been applied by Prof. A. V. Bleining⁶ in studying the moisture in clays.

Dr. John Johnston⁷ studied the dissociation pressures of several metal hydroxides and carbonates, using two experimental methods. The first was applied for hydroxides alone and is similar to one used by Brill. A small crucible containing a weighed portion (about 1.5 mg.) of the substance was suspended in a small electric furnace through which a current of air free from CO_2 and of definite vapor pressure was passed. The air was freed from CO_2 by passing through NaOH , then saturated with moisture by bubbling through a Liebig potash bulb, containing water, and



⁶ Bulletin No. 7, Bureau of Standards.

⁷ Ztschr. phys. Chem., LXII, p. 330.

was heated before passing to the furnace to prevent any condensation. The temperature of the water in the Liebig bulb was regulated by immersing it in a water bath. The furnace was held at constant temperature, and the vapor tension maintained at a definite value for 10 minutes by regulation of the water bath temperature. The crucible was then removed from the furnace and weighed on a very fine balance. Conditions of temperature and vapor pressure were so regulated that the substance maintained constant weight or gained slightly during the period, and these values were taken as the corresponding temperature and dissociation pressure of the material. The results of this method for $\text{Ca}(\text{OH})_2$ are shown in Fig. 1.

This method was found to be too slow and to frequently give inconsistent results. It was impossible to prevent the absorption of some CO_2 while removing the crucible from the furnace for weighing.

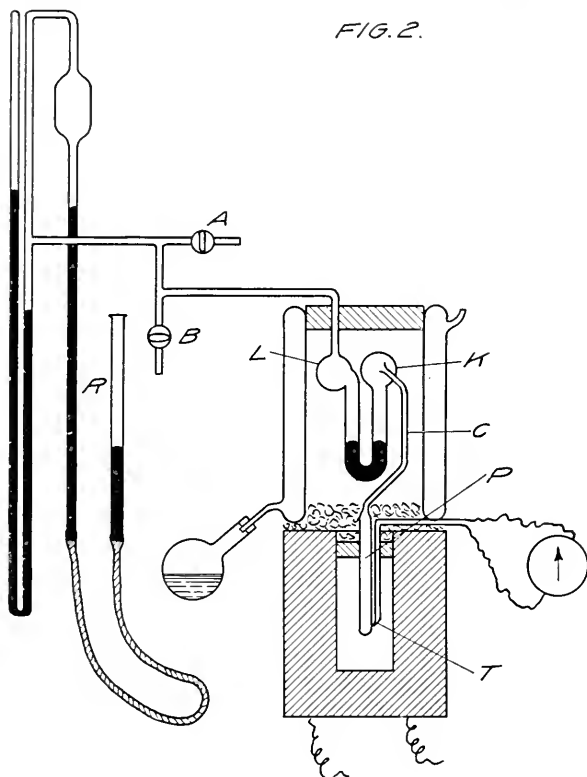
STATIC METHOD.

Dr. Johnston then resorted to the "static method," in which the dissociation pressures are measured directly. A diagram of the apparatus is shown in Fig. 2. A platinum tube, P, about 5 cm. long and 4 mm. inside diameter, contained the substance. This tube was placed in a small electric furnace with a thermocouple for determining the temperatures. A piece of glass tube, C, was fused to P and to one arm of a U tube which was connected to the barometer. On each arm of the U tube was a bulb, L, bent to the side and holding enough mercury to fill the U-tube to a depth of about 3 cm. To prevent condensation of the vapor from P, the U-tube and C were enclosed by a glass steam jacket.

With the mercury in bulb L, the apparatus was exhausted through A by means of a mercury pump. Cock A was then closed, and the mercury run from L into the U-tube by tilting the apparatus. Heating was begun, and at the first indication of pressure in P, the mercury in the two arms of the U-tube was brought to the same level by admitting some air at B and adjusting by means of the leveling tube R.

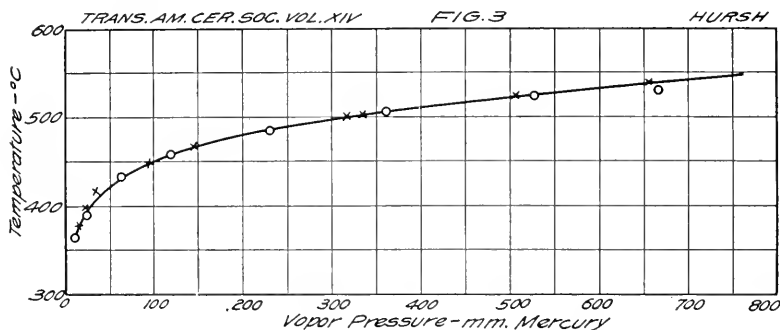
In his work with calcium hydroxide, Dr. Johnston slaked pure CaO and absorbed the excess water in a desiccator. Another portion was made by allowing the CaO to absorb moisture

FIG. 2.



slowly until the composition was about $\text{CaO } 0.8\text{H}_2\text{O}$. In using this substance, it was found necessary to heat it slightly during exhaustion of the apparatus since pressures of several cm. appeared between 200° and 300° which again disappeared in part on further heating. These abnormal pressures were supposedly due to loosely combined or absorbed moisture, and upon their appearance the test was stopped and the apparatus again exhausted. Only such pressures were taken as appeared at definite temperatures on heating and again disappeared on cooling. The "abnormal pressures" disappeared only partly on cooling. Under these conditions, it was found advisable to use a mixture of CaO and the hydroxide, although this did not entirely eliminate

the trouble, which was noted with all of the hydroxides studied. The results of the work on $\text{Ca}(\text{OH})_2$ by this method are shown in Fig. 3. By the curve, it is seen that the dissociation pressure



reaches 760 mm. at a temperature of 547°C . Hence this is taken as the dissociation temperature of the substance under atmospheric pressure.

In studying zeolites Friedel⁸ heated them at successively higher temperatures in a current of air of approximately constant vapor pressure. This method was adopted by Allen and Clement⁹ in their study of tremolite, using dry instead of moist air. A crucible containing the material was placed in an electric furnace, through which a current of air, dried by concentrated H_2SO_4 , was passed. After heating for some time at a definite temperature, the crucible was quickly removed to a desiccator, cooled and weighed. Heating was continued at each temperature until practically constant weight was obtained. In one case, the experiment was repeated with moist air to determine the effect upon the results obtained by using dry air.

EXPERIMENTAL WORK.

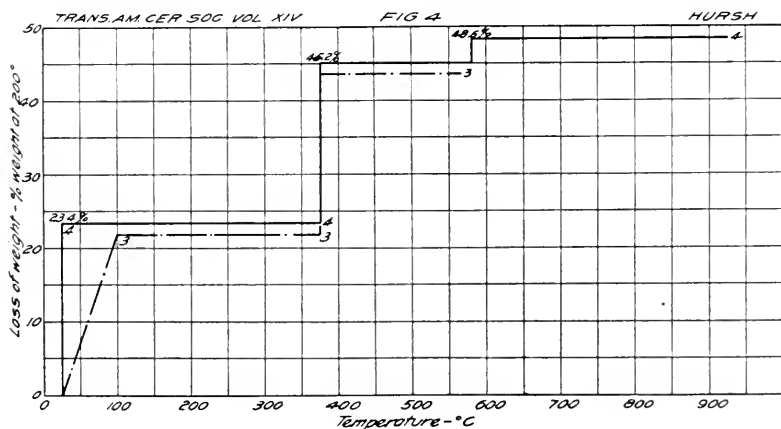
This method was adopted for the present work. The hydrate was prepared by calcining pure CaCO_3 at 1050°C . and slaking the oxide with a slight excess of water. A portion of the hydrate was placed in a platinum crucible and heated in an

⁸ Ztschr. phys. Chem., XXVI, p. 323.

⁹ Am. Jour. Sci., Vol. XXVI, No. 152.

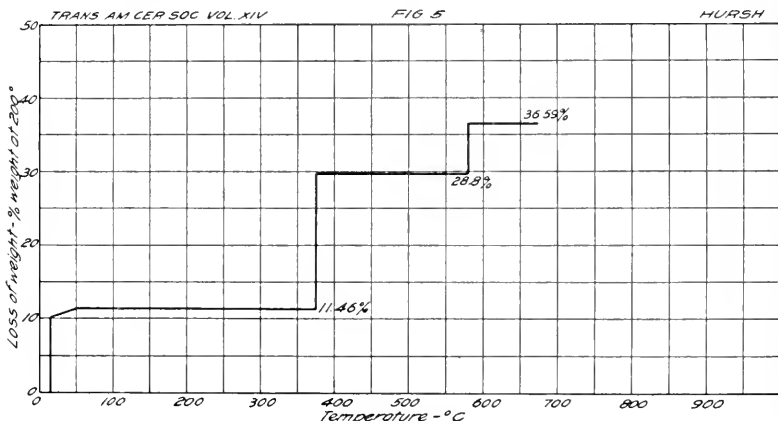
electric furnace in a bath of dry air, free from CO_2 , at successive temperatures from 200° to 750°C. at 50° intervals. At 30-minute intervals, the crucible was removed from the furnace and cooled in a desiccator over concentrated H_2SO_4 . The heating was continued at each temperature until constant weight was reached. It was impossible to prevent the absorption of some CO_2 during the transfer of the hot crucible from the furnace to the desiccator. The first loss of weight was noted at 400°C. Continued heating at this temperature gave a total loss of weight of 77 per cent. of the water present above 200°C. At 650° another loss of weight took place amounting to 22 per cent. A second trial was made with 10° intervals from 350° to 400°C. , and the first loss was found to take place at 380°C.

To prevent the absorption of CO_2 by the sample, a method of weighing within the furnace was adopted. A platinum crucible was suspended in the furnace by a fine platinum wire from one pan of a balance that was carefully protected from unequal heating from the furnace. A thermocouple was placed with the junction just under the middle of the crucible. A current of air, free from CO_2 and dried by CaCl_2 and P_2O_5 , was circulated through the furnace. A weighed portion of the hydrate was placed in the crucible and dried at 25°C. The temperature was then raised gradually until a loss of weight began at 375°C. It was somewhat surprising that there was no loss of weight be-



tween 25° and 375° as some mechanically held water might be expected. After constant weight was reached at 375° , the heating was continued beyond the point noted by Johnston. The second loss of weight took place at 580° C. The loss of weight curves for several trials are shown in Fig. 4.

To determine whether the presence of moisture in the furnace would have any effect upon the results, the air current was saturated at 0° to 1° C. before passing through the furnace, giving a vapor pressure of about 5 mm. The loss of weight was found to occur at the same points as before but to proceed at a slower rate. The quantitative results differ somewhat, due possibly to the longer time required in the latter trial. The result of the trial is shown in Fig. 5.



The results of these experiments indicate the existence of two hydrates of CaO , the $\text{CaO} \cdot \text{H}_2\text{O}$ dissociating at 375° C., leaving a lower hydrate which dissociates at 580° C., leaving CaO . That the loss of weight at each point is due to the dissociation of a chemical compound is shown by the shape of the curves. The break is abrupt with no gradual slope preceding it. If mechanical or dissolved water were being driven off, there would be a gradual loss of weight with increasing temperature.

SUMMARY.

Various temperatures are given for the dissociation of $\text{Ca}(\text{OH})_2$ ranging from 450° by Le Chatelier to 547° C. by Johnston.

Using the "loss of weight" method, two dissociation points are found. The hydrate, Ca(OH)_2 , dissociates at 375° , forming a lower hydrate that loses its H_2O at 580° C .

No mechanical water was driven off above 25° C .

In conclusion, the writer wishes to express his indebtedness to Professor A. V. Bleininger for many valued suggestions in this work.

NOTE ON THE RELATION BETWEEN PREHEATING TEMPERATURE AND VOLUME SHRINKAGE.

By R. K. HURSH.

INTRODUCTION.

An extended study of the effect of preliminary heat treatment upon clays within a practical temperature range has been made by Professor Bleining¹. Especial attention was given to the effect upon the volume shrinkage. A decided change in the properties of most of the clays was noted at temperatures of 200° to 300° C. They became more or less granular and decreased markedly in plasticity. There was a material decrease in the volume shrinkage and an increase in the amount of pore water. In a few cases, this change occurred at somewhat higher temperatures. One fine-grained, highly plastic clay, similar in behavior to bentonite, showed a considerable change in physical properties at 250°; but treatment at temperatures up to 400° failed to reduce the shrinkage to working limits.

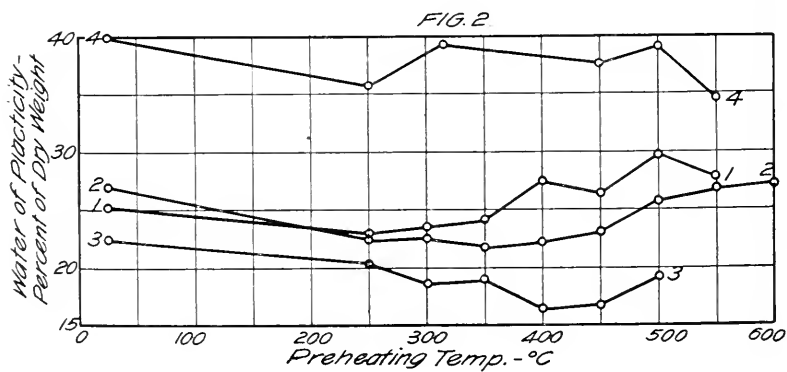
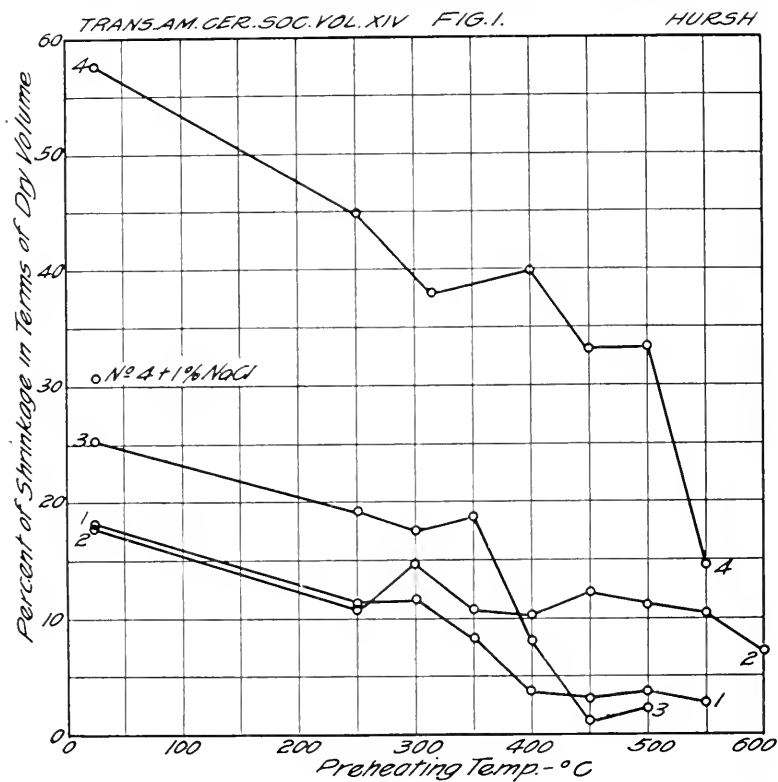
Professor Orton,² in studying some tertiary clays which gave trouble in drying, found ordinary preheating temperatures to be ineffective. When the temperature was raised to 450°-510° C. the plasticity and shrinkage were reduced sufficiently to make the clay workable. Under the conditions of the tests the period of safe treatment at these temperatures was closely limited since the clays lost their plasticity entirely when kept a little too long in the dryer. As some time is required for heat to penetrate the clay it is possible that the temperature may have reached a higher point in the longer treatments than was indicated by the thermo-couple. The test, however, represents the practical conditions in a rotary dryer.

EXPERIMENTAL WORK.

The present work was undertaken with the purpose of securing some further data upon the effect of the higher temperatures of preheating upon the physical properties of clays as indicated by changes in volume shrinkage. Four clays were used:

¹ Bull. No. 7, Bureau of Standards.

² Trans. A. C. S., Vol. XIII, p. 765.



No. 1. A plastic, somewhat sandy surface clay from Urbana, Illinois.

No. 2. A plastic, red-burning shale from Danville, Ill.

No. 3. A plastic, No. 2 fire clay, having a high drying shrinkage, from St. Louis, Mo.

No. 4. A fine grained, weathered shale from Saskatchewan similar in character to the clays studied by Professor Orton. It became very sticky in the plastic state and cracked to pieces under any conditions of drying. It is of interest to note that the addition of 1 per cent. of NaCl greatly improved the working properties and reduced the drying shrinkage nearly one-half. It would be possible by this treatment to make commercial use of the material.

The clays were heated at temperatures 50° apart from 250° to 650° C. for three hours, from 1 to 2 hours being required to reach the temperature. They were then ground to pass 20 mesh and made up into small briquets. These were weighed and the volumes measured, dried in air and at 110° in an oven, weighed, immersed in coal oil for several hours and the dry volumes measured. Care was taken to get about the same consistency in the samples when making up the briquets. The shrinkage curves are shown in Fig. 1 and the moisture content in Fig. 2.

DISCUSSION OF RESULTS.

The surface clay, No. 1, changed in color from yellow to brown at 250° and to a light salmon-red at 400° . The plasticity was considerably decreased at 250° , was very low at 400° , the briquets being very friable, and was entirely gone at 450° . The color changes seem to correspond closely to the changes in volume shrinkage. Above 300° the shrinkage decreased rapidly to 400° , beyond which the heat treatment had little effect.

The shale, No. 2, changed from gray to brown at 350° and to red at 400° . The plasticity was considerably decreased at 200° , but decreased gradually from 200° to 600° . At 650° no plasticity remained, and the briquets were too fragile to handle. The shrinkage decreases very little from 200° to 550° but drops considerably at 600° .

The fire clay, No. 3, decreased in plasticity gradually up to

400°, but at 450° it became buff in color and was practically non-plastic. The effect of the heat treatment is much more marked than with the surface clay and the shale. The shrinkage curve drops very abruptly at 350°. The behavior of this clay is similar to that of an English ball clay studied by Professor Bleining¹.

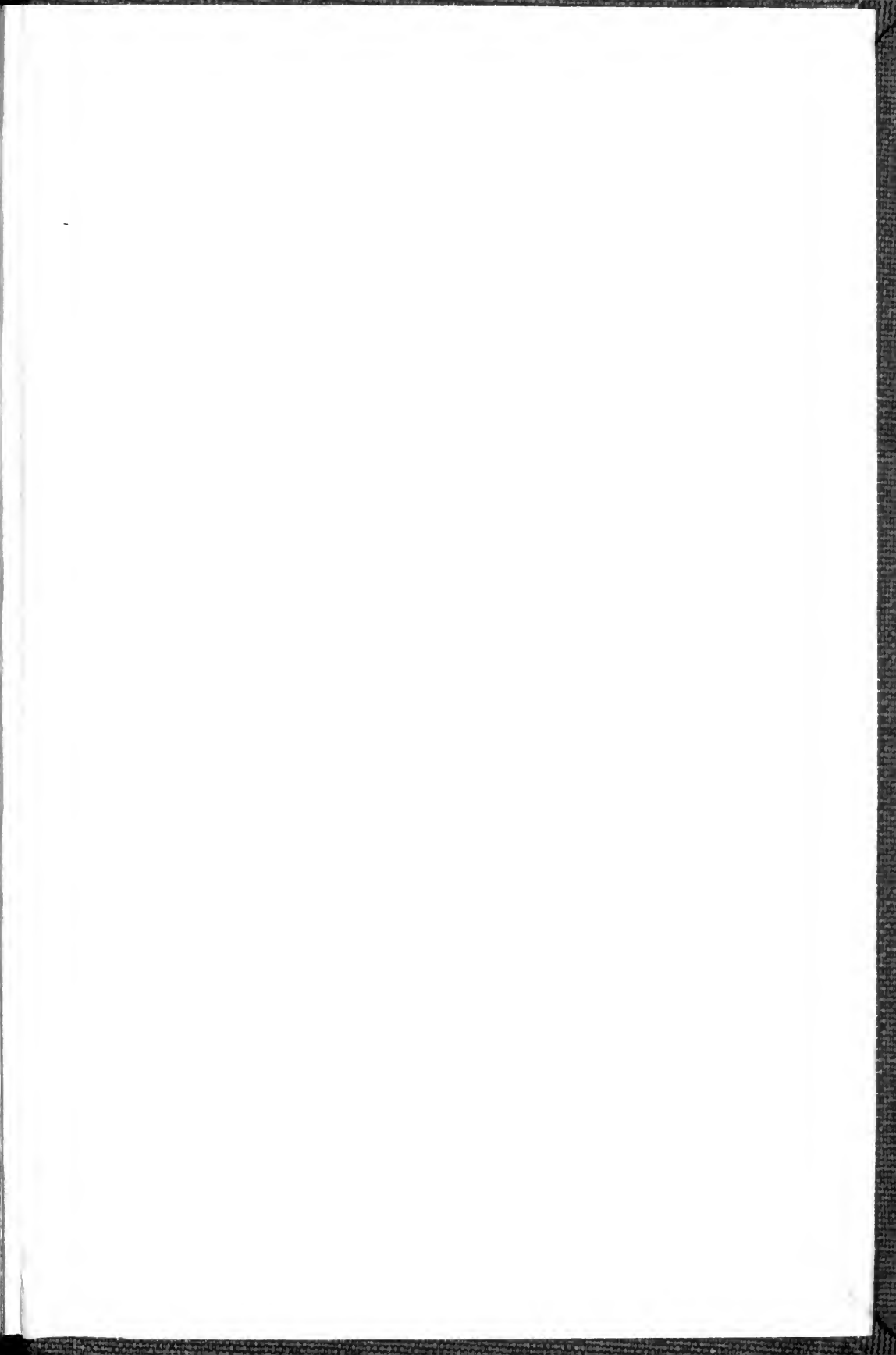
The weathered shale, No. 4, changed in color from gray to deep maroon at 330°, at which point the cracking of the briquets was noticeably decreased but was still very bad. Cracking decreased gradually beyond this temperature, but the briquets at 550° were the only ones that remained sound with open-air drying. The sticky quality of the clay was retained up to 500°. At 550° it was quite granular but developed considerable plasticity with wedging. The effect of the heating treatment upon the shrinkage is more pronounced than with the other clays, but an abnormally high shrinkage remains 500°. Beyond this point the drop in the curve is so abrupt that very careful temperature control would be necessary in obtaining a sufficient reduction in shrinkage to prevent cracking without destroying the working properties. From the high temperature required and the narrow range of safe heat treatment, it is obvious that preheating would not be a safe method for practical use with such a clay.

The effect of the heat treatment upon these clays is quite different. The shale is most gradually affected, losing its plasticity entirely only at temperatures above red heat. It is probable that this is characteristic of the more homogeneous materials.

The fire clay shows an abrupt drop in its shrinkage curve, behaving similarly to other fire clays and a certain ball clay.

The fourth clay has such abnormally high shrinkage that only treatments above 500° C. would suffice to eliminate cracking in drying. It is evident that clays of this type are not adapted to preheating treatment.





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